[4+2] Cycloaddition of *ortho*-Quinone Methides Promoted by Ionic Liquids: an Efficient and Mild Protocol for the Synthesis of Tetrahydropyranobenzopyrans

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Abstract: The stereoselective synthesis of *trans*-annelated pyrano[3,2-*c*]benzopyrans has been achieved by intramolecular [4+2] cycloaddition of *o*-benzoquinone methides that are generated *in situ* from *o*-hydroxybenzaldehydes and unsaturated alcohols using an air- and moisture-stable ionic liquid, i.e., 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 under mild and neutral conditions.

Keywords: cycloaddition; heterocycles; hetero-Diels–Alder reaction; ionic liquids (ILs); *o*-quinone methides

o-Benzoquinone methides are versatile building blocks for the construction of polycyclic ring systems, especially in the area of steroids and alkaloids having aromatic ring systems.[1] They are highly reactive and unstable intermediates in organic synthesis. This is because of the restoration of aromaticity after cycloaddition, which has been utilized for the construction of polycyclic ring systems that are otherwise difficult to synthesize.[2] They are widely used as 4π-heterodienes in inter- and intramolecular cycloaddition reactions to synthesize polycyclic oxygen heterocycles such as tetrahydrofuro- and tetrahydropyrano[3,2-*c*]benzopyrans.[3,4] The pyrano[3,2-*c*]-benzopyran skeleton is frequently found in various natural products such as flavonoids, catechins and pterocarpans.[5] *o*-Quinone methides generated *in situ* from *o*-hydroxybenzaldehydes and alkenols provide a useful entry to fused pyranobenzopyrans.[6] Generally, protic or Lewis acids are required for the *in situ* generation and subsequent cycloaddition of *o*-quinone methides. They can also be generated either by photolysis or by thermolysis of their precursors.[7,8] In recent years, ionic liquids have emerged as environmentally benign substitutes for the immobilization of transition metal-based catalysts, Lewis acids and enzymes.[9] They are being used as a set of solvents with unique properties such as tunable polarity, high thermal stability, immiscibility with a number of organic solvents, negligible vapor pressure and ease of recyclability.[10] They are referred to as 'designer solvents' as their properties such as hydrophilicity, hydrophobicity, Lewis acidity, viscosity and density can be altered by the fine-tuning of parameters such as the choice of organic cation, inorganic anion and the length of alkyl chain attached to the imidazole core (Figure 1).

These structural variations offer flexibility to the chemist to devise the best solvent that caters for and fulfills the needs of any particular process. Since ionic liquids are entirely composed of ions, they can provide an ideal reaction medium for reactions that involve reactive ionic intermediates. Due to the stabilization of charged intermediates by ionic liquids, they can provide enhanced selectivities and reaction rates. As a result of these advantages, ionic liquids are finding increasing applications in organic synthesis.[11]

In this study, we report a novel, convenient and economical protocol for the generation and subsequent cycloaddition of *o*-benzoquinone methides using the air- and moisture-stable ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF_4, under mild conditions. For instance, treatment of *o*-hydroxybenzaldehyde with 5-methyl-4-hexen-1-ol and trimethyl orthoformate in the hydrophilic ionic liquid, [bmim]BF_4 at ambient temperature afforded exclusively the *trans*-annelated pyrano[3,2-*c*]benzopyran **3** in 89% yield (Scheme 1).

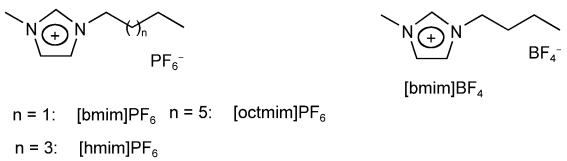
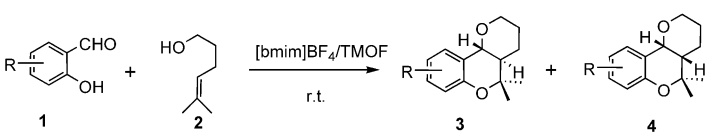


Figure 1. Chemical structures of ionic liquids.



Scheme 1.

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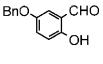
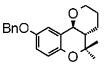
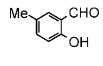
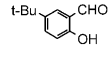
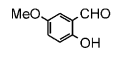
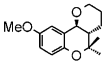
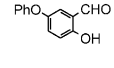
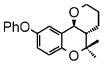
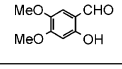
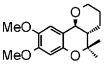
In a similar fashion, several substituted *o*-hydroxybenzaldehydes reacted smoothly with 5-methyl-4-hexen-1-ol to afford the corresponding *trans*-fused pyranobenzopyrans in high yields. In all cases, the reactions proceeded efficiently at room temperature with high diastereoselectivity. Only a single diastereomer was obtained in each reaction, the structure of which was established by ^{1}H, ^{13}C NMR spectroscopy and mass spectrometry. The assigned structure was further confirmed by direct comparison with known compounds.[6] The reactions are clean, diastereoselective and complete within 3–6 h. In the absence of ionic liquid, the reaction did not proceed in polar organic solvents such as dichloromethane, acetonitrile, methanol, DMF and DMSO. The presence of acid catalyst was essential for the success of the reaction in organic solvents. The reaction is highly diastereoselective with salicylaldehydes and 5-methyl-4-hexen-1-ol and the products are obtained in excellent yields. Since the products were fairly soluble in the ionic phase, [bmim]BF_4, they could be easily separated by simple extraction with diethyl ether. The recovered ionic liquid was reused for subsequent reactions with a gradual decrease in activity. However, the products were obtained in the same purity as in the first run in runs carried out using recycled ionic liquid. For instance, treatment of salicylaldehyde with 5-methyl-4-hexen-1-ol in hydrophilic [bmim]BF_4 gave 89%, 86% 83% and 80% yields over four cycles. Among various ionic liquids such as [bmim]PF_6, [hmim]PF_6, and [octmim]PF_6, [bmim]BF_4 was found to be superior in terms of conversion. Ionic liquids used in this study were procured from Fluka and used without any further purification. The purity of [bmim]PF_6 is $\geq$97.0% (by NMR).

There are several advantages in the use of ionic liquids as the promoter for this transformation, which include high conversions, mild reaction conditions, short reaction times, simplicity in operation and recyclability of ionic liquids (ILs). The reaction may proceed through an intramolecular [4+2] cycloaddition of *o*-benzoquinone methides that are formed *in situ* from *o*-hydroxybenzaldehydes and unsaturated alcohols in the ionic liquid as shown in Scheme 2.

The scope and generality of this process is illustrated with respect to various substituted *o*-hydroxybenzaldehydes and 5-methyl-4-hexen-1-ol and the results are presented in Table 1.

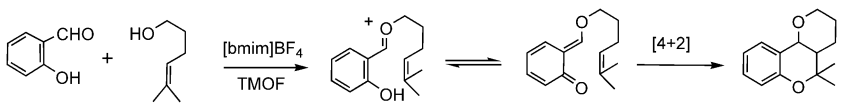
In conclusion, we describe ionic liquids (ILs) as novel and recyclable solvents for the stereoselective synthesis of *trans*-fused pyranobenzopyrans by an intramolecular [4+2] cycloaddition of *o*-benzoquinone methides that are generated *in situ* from *o*-hydroxybenzaldehydes and unsaturated alcohols under mild conditions. The simple operation combined with ease of recovery and reuse of this novel reaction medium makes this process economic, benign and a waste-free route for the synthesis of *trans*-annelated pyrano[3,2-*c*]benzopyrans. The use of ionic liquids as promoters for this transformation helps to avoid the use of corrosive, toxic and heavy metal Lewis acids.

Table 1. The [bmim]BF_4-promoted synthesis of pyrano[3,2-*c*]-benzopyrans.

Entry	*o*-Hydroxybenzaldehyde	Product[a]	Reaction time [h]	Yield [%][b]
a			4.5	89
b			4.0	90
c			4.5	88
d			5.0	85
e			4.0	87
f			5.0	82
g			6.0	80
h			3.5	86
i			3.0	89
j			3.5	87
k			4.5	80
l			3.5	85
m			4.0	91

[a] All products were characterized by ^{1}H, ^{13}C NMR, IR and mass spectrometry.

[b] Yield refers to pure products after column chromatography.



Scheme 2.

Experimental Section

General Remarks

Melting points were recorded on a Büchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded on a Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

General Procedure for the Preparation of *trans*-Annelated Pyranobenzopyrans

A mixture of *o*-hydroxybenzaldehyde (2 mmol), 5-methyl-4-hexen-1-ol (2 mmol), trimethyl orthoformate (3 mmol) and [bmim]BF_4 (3 mL) was stirred at room temperature for the appropriate time (Table 1). After complete conversion as indicated by TLC, the reaction mixture was extracted twice with diethyl ether (2×10 mL). The combined ether extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting product was purified by column chromatography on silica gel (Merck, 100–200 mesh, ethyl acetate-hexane, 1:9) to afford the pure pyrano[3,2-*c*]benzopyran. The recovered ionic liquid was reused for subsequent runs.

***trans*-5,5-Dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano-[3,2-*c*]-1-benzopyran (3a):** Colorless solid, mp 65–67 °C,; IR (KBr): $\nu = 3035, 2970, 1617, 1580, 1105, 1075\ cm^{-1}$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ (s, 3H), 1.36–1.39 (m, 1H), 1.40 (s, 3H), 1.70–1.85 (m, 3H), 1.95–2.05 (m, 1H), 3.65 (dt, 1H, $J = 3.5$, 11.5 Hz), 4.18 (dd, 1H, $J = 5.0$, 11.5 Hz), 4.20 (d, 1H, $J = 10.5$ Hz), 6.78 (d, 1H, $J = 8.0$ Hz), 6.93 (t, 1H, $J = 7.8$ Hz), 7.18 (t, 1H, $J = 8.0$ Hz), 7.40 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.3$, 24.9, 26.3, 27.5, 45.2, 68.2, 73.7, 78.2, 116.7, 119.9, 122.5, 126.0, 128.8, 152.6; EIMS: $m/z = 218$ (M^+), 200, 186, 163, 146, 96, 68, 55, 41.

***trans*-5,5-Dimethyl-7-methoxy-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3b):** Pale yellow solid, mp 96–97 °C; IR (KBr): $\nu = 3038$, 2975, 1615, 1585, 1107, 1070 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$ (s, 3H), 1.33–1.37 (m, 1H), 1.40 (s, 3H), 1.67–1.80 (m, 3H), 1.90–2.05 (m, 1H), 3.63 (dt, 1H, $J = 3.8$, 11.5 Hz), 3.85 (s, 3H), 4.15 (dd, 1H, $J = 4.8$, 11.6 Hz), 4.23 (d, 1H, $J = 10.3$ Hz), 6.70 (dd, 1H, $J = 2.8$, 8.2 Hz), 6.80 (t, 1H, $J = 7.8$ Hz), 7.05 (d, 1H, $J = 8.2$ Hz); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.1$, 25.0, 26.4, 27.3, 29.8, 46.8, 56.3, 68.7, 73.5, 78.0, 103.1, 110.2, 129.4, 155.0, 160.2; EIMS: $m/z = 248$ (M^+), 234, 217, 166, 147, 138, 109, 96, 69, 55, 41.

***trans*-5,5-Dimethyl-7-ethoxy-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3c):** Colorless liquid; IR (KBr): $\nu = 3040$, 2968, 1616, 1585, 1120, 1070 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 3H), 1.38–1.14 (m, 1H), 1.45 (t, 3H, $J = 6.8$ Hz), 1.48 (s, 3H), 1.70–1.83 (m, 3H), 1.97–2.05 (m, 1H), 3.65 (dt, 1H, $J = 3.7$, 11.6 Hz), 4.15 (q, 2H, $J = 6.8$ Hz), 4.18 (dd, 1H, $J = 5.0$, 11.6 Hz), 4.25 (d, 1H, $J = 10.5$ Hz), 6.78 (dd, 1H, $J = 2.7$, 8.0 Hz), 6.80 (t, 1H, $J = 7.8$ Hz), 7.08 (d, 1H, $J = 8.0$ Hz); ^{13}C NMR (75 MHz, proton decoupled, $CDCl_3$): $\delta = 14.7$, 20.2, 24.9, 26.1, 27.3, 44.9, 65.0, 68.1, 73.6, 78.3, 104.0, 118.3, 119.15, 123.3, 143.2, 147.3; EIMS: $m/z = 262$ (M^+), 248, 204, 166, 138, 109, 97, 81, 69, 55, 41.

***trans*-9-Benzyloxy-5,5-dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3d):** Pale yellow oil; IR (KBr): $\nu = 3037$, 2960, 1610, 1580, 1115, 1083 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$ (s, 3H), 1.30–1.37 (m, 1H), 1.42 (s, 3H) 1.75–1.83 (m, 3H), 1.95–2.05 (m, 1H), 3.65 (dt, 1H, $J = 3.5$, 11.7 Hz), 4.18 (dd, 1H, $J = 4.8$, 11.7 Hz), 4.21 (d, 1H, $J = 10.4$ Hz), 5.05 (s, 2H), 6.70 (d, 1H, $J = 8.2$ Hz), 6.83 (dd, 1H, $J = 2.7$, 8.2 Hz), 7.09 (d, 1H, $J = 2.7$ Hz), 7.35–7.48 (m, 5H); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.2$, 25.1, 26.3, 27.5, 45.2, 68.2, 70.7, 73.7, 77.9, 111.3, 116.6, 117.4, 122.8, 127.4, 127.6, 128.3, 137.5, 146.9, 152.6; EIMS: $m/z = 324$ (M^+), 234, 216, 187, 149, 91, 55, 43.

***trans*-5,5,9-Trimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano-[3,2-*c*]-1-benzopyran (3e):** Colorless liquid, IR (KBr): $\nu = 3038$, 2965, 1615, 1578, 1128, 1080 cm.$^{-1}$ ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.18$ (s, 3H), 1.30–1.37 (m, 1H), 1.38 (s, 3H), 1.65–1.78 (m, 3H), 1.88–1.97 (m, 1H), 2.25 (s, 3H), 3.60 (dt, 1H, $J = 3.7$, 11.8 Hz), 4.10 (dd, 1H, $J = 5.0$, 11.8 Hz), 4.18 (d, 1H, $J = 10.5$ Hz), 6.60 (d, 1H, $J = 8.2$ Hz), 6.90 (dd, 1H, $J = 2.8$, 8.2 Hz), 7.18 (d, 1H, $J = 2.7$ Hz). ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.0$, 20.3, 24.9, 26.1, 27.3, 45.1, 68.0, 73.5, 77.7, 116.2, 121.9, 126.0, 128.6, 129.2, 150.3. EIMS: $m/z = 232$ (M^+), 217, 173, 159, 136, 121, 98, 69, 55, 41.

***trans*-9-(*tert*-butyl)-5,5-dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-c]-1-benzopyran (3f):** Oily liquid; IR (KBr): $\nu = 3043$, 2963, 1620, 1570, 1128, 1075 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$ (s, 3H), 1.30 (s, 9H), 1.32–1.38(m, 1H), 1.40 (s, 3H), 1.67–1.80 (m, 3H), 1.90–1.98 (m, 1H), 3.63 (dt, 1H, $J = 3.5$, 11.4 Hz), 4.18 (dd, 1H, $J = 4.8$, 11.4 Hz), 4.20 (d, 1H, $J = 10.3$ Hz), 6.65 (d, 1H, $J = 8.0$ Hz), 7.18(dd, 1H, $J = 2.5$, 8.0 Hz), 7.40 (d, 1H, $J = 2.5$ Hz); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.4$, 25.2, 26.3, 27.6, 31.6, 34.1, 45.3, 68.2, 73.8, 77.9, 116.1, 121.5, 122.3, 125.8, 142.4, 150.4; EIMS: $m/z = 274$ (M^+), 259, 217, 163, 146, 97, 84, 69, 55, 41.

***trans*-5,5-Dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano-[3,2-*c*]-1-benzo[*f*]-1-benzopyran (3 g):** Brown solid; mp 112–113 °C; IR (KBr): $\nu = 3040$, 2967, 1618, 1580, 1125, 1075 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (s, 3H), 1.38–1.43 (m, 1H), 1.45 (s, 3H) 1.70–1.85 (m, 3H), 1.97–2.05 (m, 1H), 3.80 (dt, 1H, $J = 3.7$, 11.6 Hz), 4.18 (dd, 1H, $J = 5.0$, 11.6 Hz), 4.58 (d, 1H, $J = 9.8$ Hz), 6.97 (d, 1H, $J = 8.7$ Hz), 7.30 (t, 1H, $J = 7.8$ Hz), 7.38 (t, 1H, $J = 7.8$ Hz), 7.65 (d, 1H, $J = 8.7$ Hz), 7.70 (d, 1H, $J = 7.8$ Hz), 8.20 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (75 MHz, proton decoupled, $CDCl_3$): $\delta = 19.0$, 25.6, 26.6, 27.2, 46.9, 68.2, 74.6, 78.1, 113.3, 119.3, 122.9, 125.1, 125.9, 128.0, 129.3, 130.0, 132.5, 151.6; EIMS: $m/z = 270$ (M^+), 254, 196, 173, 145, 115, 84, 41.

***trans*-5,5-Dimethyl-9-isopropyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3 h):** Yellow liquid; IR (KBr): $\nu = 3045$, 2961, 1617, 1583, 1117, 1080 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.80$ (d, 6H, $J = 7.0$ Hz), 1.23 (s, 3H), 1.32–1.37 (m, 1H), 1.39 (s, 3H) 1.65–1.77 (m, 3H), 1.90–1.97 (m, 1H), 2.80 (m, 1H), 3.60 (dt, 1H, $J = 3.5$, 11.5 Hz), 4.17 (dd, 1H, $J = 4.9$, 11.5 Hz), 4.19 (d, 1H, $J = 10.0$ Hz), 6.60 (d, 1H, $J = 8.2$ Hz), 6.98 (dd, 1H, $J = 2.7$, 8.2 Hz), 7.20 (d, 1H, $J = 2.7$ Hz); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): $\delta = 20.4$, 24.0, 24.3, 25.1, 26.2, 27.6, 33.4, 45.2, 68.2, 73.8, 77.9, 116.4, 121.9, 123.5, 126.7, 140.1, 150.6; EIMS: $m/z = 260$ (M^+), 246, 218, 149, 98, 71, 55.

***trans*-5,5-Dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-[1,3]dioxolo[5,4-*g*]pyrano[3,2-*c*]-1-benzopyran (3i):** Colorless oil, IR

(KBr): ν = 3025, 2968, 1580, 1510, 1138, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 3H), 1.30–1.35 (m, 1H), 1.37 (s, 3H), 1.60–1.78 (m, 3H), 1.85–1.93 (m, 1H), 3.58 (dt, 1H, *J* = 3.5, 11.5 Hz), 4.05 (dd, 1H, *J* = 5.0, 11.5 Hz), 4.18(d, 1H, *J* = 10.2 Hz), 5.82 (s, 2H), 6.25 (s, 1H), 6.80 (s, 1H); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): δ = 20.0, 25.0, 26.4, 27.5, 45.2, 68.2, 74.0, 78.3, 98.4, 100.8, 105.1, 113.4, 140.5, 147.3, 147.7; EIMS: *m/z* = 262 (M^+), 243, 200, 186, 163, 146, 96, 68, 55, 41.

***trans*-5,5-Dimethyl-9-methoxy-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3j):** Yellow solid; mp 54–56 °C; IR (KBr): ν = 3038, 2975, 1616, 1587, 1107, 1070 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.32–1.37 (m, 1H), 1.43 (s, 3H), 1.76–1.84 (m, 3H), 1.89–1.97 (m, 1H), 3.61 (dt, 1H, *J* = 3.7, 11.7 Hz), 3.90 (s, 3H), 4.17 (dd, 1H, *J* = 4.9, 11.7 Hz), 4.20 (d, 1H, *J* = 10.3 Hz), 6.60 (d, 1H, *J* = 7.9 Hz), 6.85 (dd 1H, *J* = 2.1, 7.9 Hz), 7.10 (d, 1H, *J* = 2.1 Hz); ^{13}C NMR (50 MHz, proton decoupled, $CDCl_3$): δ = 20.1, 25.0, 26.4, 27.3, 29.8, 46.8, 56.3, 68.7, 73.5, 78.0, 103.1, 110.2, 129.4, 155.0, 160.2; EIMS: *m/z* = 248 (M^+), 234, 217, 189, 152, 138, 109, 97, 69, 55, 41.

***trans*-5,5-Dimethyl-9-bromo-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3k):** Yellow oil; IR (KBr): ν = 3040, 2968, 1585, 1508, 1133, 1089 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.18 (s, 3H), 1.35–1.39 (m, 1H), 1.40 (s, 3H), 1.65–1.80 (m, 3H), 1.90–2.0 (m, 1H), 3.60–3.63 (m, 1H), 4.15–4.20 (m, 1H), 4.20 (d, 1H, *J* = 10.5 Hz), 6.60 (d, 1H, *J* = 8.3 Hz), 7.21 (dd, 1H, *J* = 2.7, 8.3 Hz), 7.50 (d, 1H, *J* = 2.7 Hz); EIMS: *m/z* = 299, 297 (M^+), 217, 149, 98, 69, 55, 41.

***trans*-5,5-Dimethyl-9-phenoxy-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3 l):** Pale yellow oil; IR (KBr): ν = 3040, 2970, 1610, 1580, 1130, 1078 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.35–1.38 (m, 1H), 1.40 (s, 3H), 1.65–1.80 (m, 3H), 1.90–1.98 (m, 1H), 3.60 (dt, 1H, *J* = 3.8, 11.8 Hz), 4.15 (dd, 1H, *J* = 5.0, 11.8 Hz), 4.20 (d, 1H, *J* = 10.5 Hz), 6.70 (d, 1H, *J* = 8.0 Hz), 6.80 (dd, 1H, *J* = 2.5, 8.0), 6.85–6.97 (m, 3H), 7.08 (d, 1H, *J* = 2.5 Hz), 7.18–7.20 (m, 2H); EIMS: *m/z* = 310 (M^+), 234, 217, 95, 81, 69, 55, 41.

8,9-Dimethoxy-5,5-dimethyl-3,4,4a,10b-tetrahydro-2*H*,5*H*-pyrano[3,2-*c*]-1-benzopyran (3 m): Brown solid; mp 51–52 °C; IR (KBr): ν = 3038, 2975, 1616, 1587, 1107, 1070 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.32–1.37 (m, 1H), 1.42 (s, 3H), 1.76–1.84 (m, 3H), 1.89–1.97 (m, 1H), 3.61 (dt, 1H, *J* = 3.7, 11.5 Hz), 3.80 (s, 6H), 4.05 (dd, 1H, *J* = 5.0, 11.5 Hz), 4.18 (d, 1H, *J* = 10.2 Hz), 6.30 (s, 1H), 6.85 (s, 1H); EIMS: *m/z* = 278 (M^+), 264, 247, 234, 189, 138, 109, 97, 69, 55, 41.

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